THERMODYNAMICS OF REACTIONS INVOLVING H_2O AND HYDROCARBON RADICALS BETWEEN 27 AND 374°C

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Hydrous pyrolysis experiments at temperatures between 300 and 360°C for 72 hours have shown that H_2O is a source of oxygen and hydrogen in the generation of oil from petroleum source rocks. Oxygen mass-balance calculations indicate that the only source of the calculated excess oxygen in the form of CO_2 is H_2O (Lewan, 1992; Seewald, 1994). Experiments with D_2O instead of H_2O show that generated hydrocarbons are highly deuterated (Hoering, 1984), which is interpreted as being the result of D_2O-derived deuterium quenching free-radical sites as the organic matter in a petroleum source rock thermally decomposes (Lewan, 1997).

Hydrous pyrolysis experiments are typically conducted with crushed gravel-sized (0.5 to 2.0 cm) source rock, which is heated in contact with liquid H_2O at subcritical temperatures (<374°C). Initially, the maturing source rock gravel is impregnated with polar-rich bitumen that partially decomposes with increasing thermal stress to yield an expelled saturate-rich oil. As demonstrated by Lewan (1997), the reaction of H_2O with the organic matter occurs within the hydrophobic bitumen-impregnated rock and not in the liquid H_2O that surrounds the rock gravel. Therefore, the reaction involves dissolved H_2O in the bitumen of the rock and not aqueous organic species in the surrounding liquid water. It has been proposed that the H_2O dissolved in the bitumen ($H_2O_{(bit)}$) of a source rock reacts with free radical sites to generate aldehydes, alcohols, alkanes, hydrogen, or oxygen. The model reactions include the following:

$$C_nH_{2n+1(bit)}^{\bullet} + H_2O_{(bit)} \Leftrightarrow C_nH_{2n}O_{(bit)} + 1.5\,H_{2(bit)} \qquad \text{[Reaction I]}$$

$$C_nH_{2n+1(bit)}^{\bullet} + H_2O_{(bit)} \Leftrightarrow C_nH_{2n+1}OH_{(bit)} + 0.5\,H_{2(bit)} \qquad \text{[Reaction II]}$$

$$2\,C_nH_{2n+1(bit)})^{\bullet} + H_2O_{(bit)} \Leftrightarrow 2\,C_nH_{2n+2(bit)} + 0.5\,O_{2(bit)} \qquad \text{[Reaction III]}$$

Although it is uncertain whether these model reactions have kinetic energy barriers to overcome, the first concern is whether they are thermodynamically possible within the experimental conditions. Unfortunately, thermodynamic data on alkyl radicals, H_2O, and the proposed products in a bituminous phase are not currently available. However, a first approximation of the thermodynamic feasibility of these model reactions can be obtained by considering the reactions in a gaseous phase for which thermodynamic data are available.

Gibbs free energies for these reactions in the gaseous phase where n = 2 were calculated from tabulated standard-state (25°C at 100 kPa) heat capacities given by Benson (1976) and Gurvich et al. (1994) for temperatures between 27 and 374°C. As shown in Figure 1, the resulting Gibbs free energy of reaction between 0 and 400°C at 100 kPa for Reactions I, II, and III are -10.5 to -13.5 kcal/mol, -18.8 to -11.9 kcal/mol, and -27.3 to -17.8 kcal/mol, respectively. These negative values indicate that the model reactions for n = 2 are thermodynamically favorable in this temperature range at hydrogen or oxygen fugacities of 100 kPa or less.

Reaction I involves oxygen from a water molecule reacting with an unpaired electron at an alkyl radical site to form an aldehyde and hydrogen. The hydrogen would be available to react with other free radical sites and the aldehyde would react with other water molecules to form a carboxylic acid and through subsequent decarboxylation form CO_2. Each molecule of water that reacts with a free radical site by this reaction,

generates three atoms of hydrogen that can terminate or initiate additional free radical sites. A subsequent reaction of the resulting aldehyde with other water molecules yields two additional hydrogen atoms by the reaction

$$R\text{–}\underset{H}{C}=O + H_2O_{(bit)} \rightarrow RH + CO_{2(bit/g)} + H_{2(bit/g)}, \qquad \text{[Reaction IV]}$$

where R is an alkyl or aryl group in macromolecules of the organic matter. The interaction of water with carbonyl groups has been suggested to be responsible for increased CO_2 yields associated with the weathering of coal in water vapor at low temperatures (150°C; Peitt, 1991) and the noncatalytic liquefaction of water-treated coals at 350°C (Song et al., 1994). As a result, reactions I and IV may collectively generate 5 water-derived hydrogen atoms for every water-derived oxygen that reacts with a free radical site.

Alcohols have not been reported in the products of hydrous pyrolysis experiments as prescribed by reaction II. However, Stalker et al. (1994) have reported the generation of phenols from water-derived oxygen in $H_2{}^{18}O$-experiments with kerogen at 300°C after 72 hours. Smith et al. (1989) observed that hydrous pyrolysis of n-octadecanol in the presence of coal completely reacts to form n-alkanes at 330°C after 72 hours. Therefore, it is reasonable to tentatively suggest that alcohols derived from reaction II may be ephemeral intermediates in the formation of alkanes.

Reaction III is the most thermodynamically favorable reaction of the three model reactions. Molecular oxygen generated from this reaction would be highly reactive and prone to generate or terminate other free-radical sites. Eventually, this oxygen would occur as a carbonyl, carboxyl, or CO_2 through a series of subsequent reactions. The significance of the thermodynamic favorability of reaction III is demonstrated by comparing its low Gibbs energy of reaction with that of the thermodynamically unfavorable reaction of H_2O with ethene to form an ethane (Figure 1):

$$C_2H_{4(g)} + H_2O_{(g)} \Leftrightarrow C_2H_{6(g)} + 0.5\ O_{2(g)} \qquad \text{[Reaction V]}$$

It is not the intent of this discussion to suggest that reactions I, II, and III are specific reactions that occur in petroleum formation, but rather they simply serve to demonstrate that reactions between alkyl free-radical sites and water in gaseous phases are thermodynamically favorable between 27 and 374°C at 100 kPa. A more specific thermodynamic evaluation of the feasibility of these model reactions requires obtaining thermodynamic parameters on H_2O as a dissolved species in bitumen or oil solvents. Once these parameters have been determined, the competition between $H_2O_{(bit)}$ and $H_{2(bit)}$ for alkyl free-radical sites can be properly assessed.

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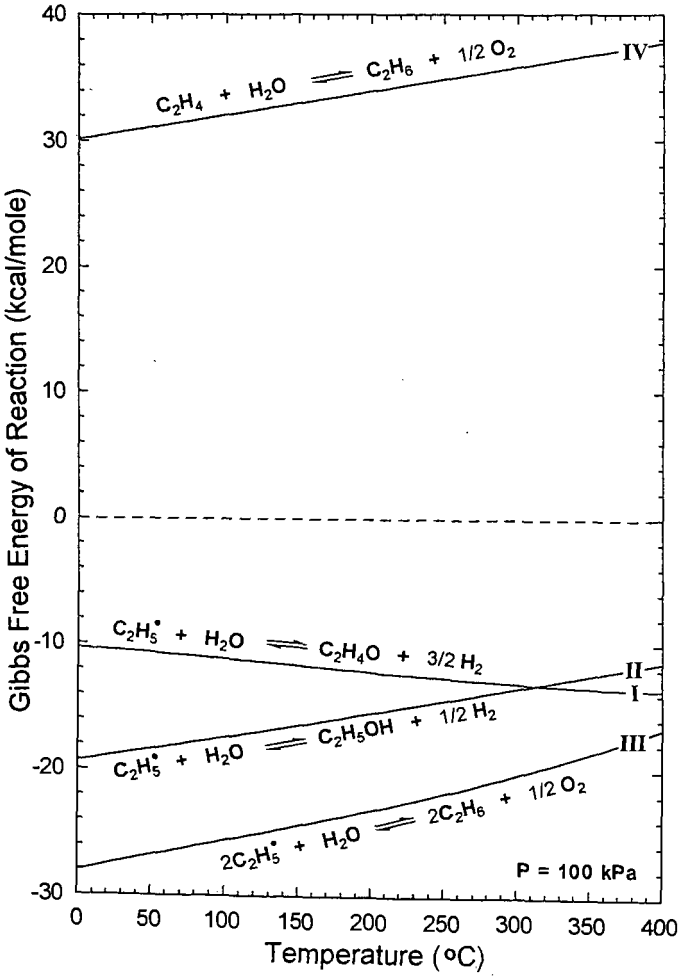

Figure 1. Gibbs free energy of reaction for model reactions I, II, III, and IV for various temperatures at 100 kPa.